Correlation of in-situ Raman spectra with isothermal DSC-measurements on radically polymerizing methyl methacrylate

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Abstract

This work discusses the capability of Raman spectroscopy in monitoring the cure reaction and conversion of methyl methacrylate (MMA) in comparison to the conventional differential scanning calorimetry (DSC). In this regard, isothermal DSC measurements have been carried out as standard and compared against in-situ Raman spectra with the same material composition. A novel sample holder has been designed and implemented within the heated Raman chamber to monitor the cure reaction of the highly volatile MMA. The resulting spectra were processed using a custom written Python script, to compare the most significant C=C and C=O peaks. The conversion of monomeric MMA to Poly(methyl methacrylate) (PMMA) was calculated via the relative peak intensity of C=O at 1725 cm^{-1} to C=C at 1640 cm^{-1}. Small deviations between the different measurement techniques have been observed and discussed in detail. The fundamental principle of Raman based in-situ conversion monitoring is proposed for industrial manufacturing of PMMA. Since these Raman measurements are carried out between 2 transparent glass plates, that are unaffected by the laser used, a simple and analogous setup would suffice industrially for on-line quality control and process optimization.

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1. Introduction

The main application of Polymethylmethacrylate (PMMA) is in the form of sheets and panes in varying thicknesses. Since 1933, this transparent polymer is distributed for affordable transparent lightweight applications [1], although widespread requests in the medical sector [2], for instance in enzyme immobilization [3] or as artificial bone cement for joint replacements [4], as well as in dentistry [5], arose over time. The synthesis of PMMA is mainly carried out as radical polymerization, although anionic and living polymerizations sometimes find application as well. [6, 7] To form plates of PMMA, two main methods are used in industrial settings. The first one is extrusion of pre-polymerized PMMA granules, that can be produced by emulsion and solution polymerization. [1] The other is by pouring the monomer initiator mixture into a mould, made of paralelly placed glass panes, and carry out an in situ bulk polymerization. [1] Latter often generates, due to the extreme smoothness of glass panes, products with a higher optical grade and shall therefore be considered as subject of the following discussion.

As commonly known from most polymer forming chain reactions, an auto acceleration takes place in bulk. This so called Trommsdorff effect is due to the exothermic character of polymerization, as well as the increase in viscosity, and can lead to teamperatures that might cause damage to the polymer itself. Therefore PMMA, especially for optical applications, has to be monitored and carefully polymerized to avoid any influence on the visual appearance, i.e. yellowing or other optical defects such as streaks. [8]

It is crucial, that either very good process knowledge of the system in use has to be available, or a strict monitoring of the reaction status and velocity must be carried out, to avoid too vigorous Trommsdorff effect. One possibility is the placement of thermocouples in the monomer mixture as *Suzuki et al.* showed in [9], though this leads to unsellable material at the edges in terms of industrial applications. Thermocouples in contact with the glass panes from the outside, unlike with MMA, might not indicate the exact temperature of the mixture and underlay a timeshift due to the glass's thermal insulating capabilities. Hence, a way of monitoring the reaction status without contacting the mixture is therefore desireable. IR-measurements would be able to deliver a decent overview over the monomer conversion, as *Darcos et al.* showed in [10], though the used float glass panes are not IR transparent and special windows for monitoring points are needed. The high volatility of MMA generates the need for special care on sealing of the sensors, too.

On the other hand, Raman spectroscopy, depending on the used laser's wavelength, is unaffected by the glass panes. Considering the work of *Pallikari et al.*, conversion

determination based on Raman seems to be feasable [11]. The use of C=O stretching at 1725 cm^{-1} and C=C stretching at 1640 cm^{-1} in their work showed the possible potential, given the fact that the samples were polimerized separately and the reaction state frozen via dropping the mixture into liquid nitrogen [11]. To prove the general applicability of this technique as in-situ measurement, this work focuses on the design of a Raman spectrometer sample holder for volatile liquids that can be heated to measure the conversion of MMA to PMMA while polymerization. Additionally, the change in the spectra will be deconvoluted with a customized Python script and the conversion over time compared to DSC measurements for validation. The applicability of DSC in conversion and kinetics detection on PMMA has been shown by *Jašo et al.* [12], and hence finds application in this paper as a reference method.

2. Materials and Methods

2.1 Material composition

As base material for the tests carried out in this paper, a mixture of monomeric MMA, p-Methoxyphenole (MEHQ) inhibitor and different radical-forming azo-compounds as initiator have been provided by *KRD Coatings GmbH*. Since the mixture is part of an ongoing project underlying a non-disclosure agreement, the exact composition has to remain undisclosed, though is not of importance for the evaluations and conclusions drawn in this paper.

2.2 Testing methods and parameters

The Raman measurements have been carried out with a *Senterra* spectrometer from *Bruker*, which utilizes a microscope with 20x magnification, in order to be able to focus inside the sample holders liquid chamber. As source for the Raman excitation, a 532 nm laser was tuned to 20 mW. Sampling was carried out between 1510 cm^{-1} and 2740 cm^{-1} four times over a timespan of 10 seconds. The heating of the sample holder to the desired reaction temperature of 70 °C was achieved with a *Linkam FTIR600* heatbed, placed inside the Ramans microscopy apparatus. The sample holder itself contains four distinctive parts shown in *Figure 1*:

1. The copper lid, to keep the upper sealing closed during the tests.
2. The transparent chamber sealing, accomplished by o-rings and Raman-transparent float glass panes.
3. The copper centre part, which acts sample chamber.
4. The heat conductive copper bottom plate, which is meant to be the base for the other compontens.

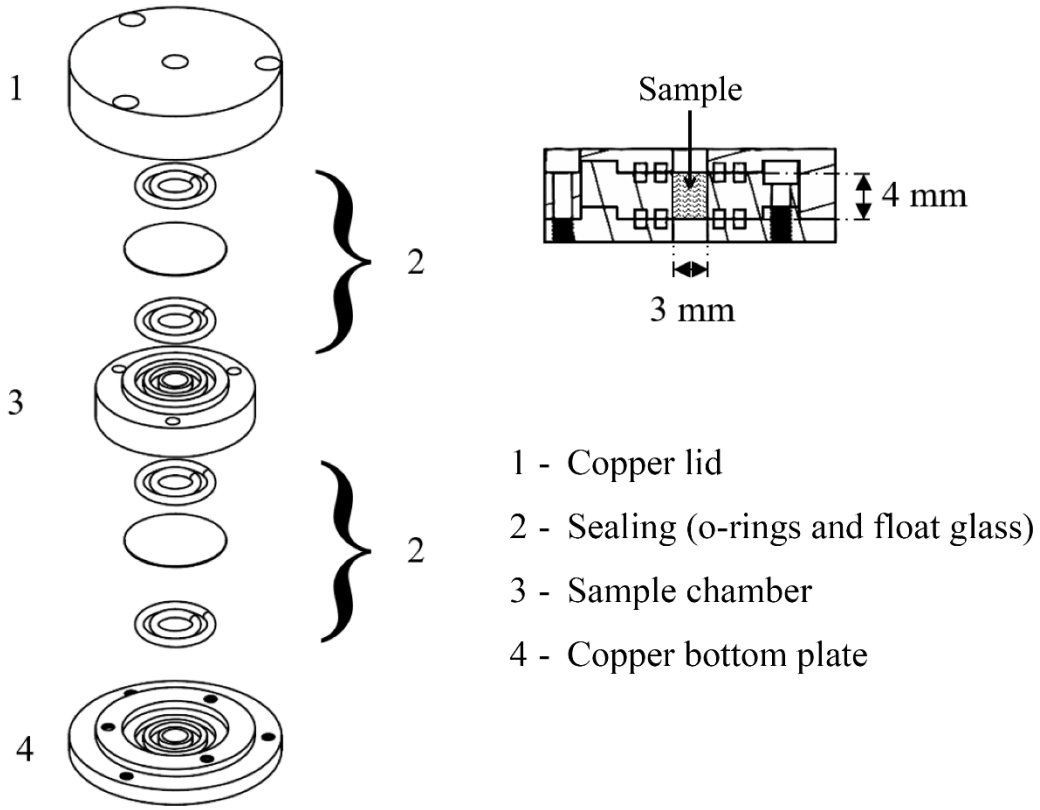

Figure 1: Schematics of the sample holder - left: exploded view, right: assembled view (central sample area filled with a wavelike pattern)

Dynamic Scanning Calorimetry (DSC) was carried out with a *DSC-Q2000* from *TA Instruments*, calibrated with an Indium standard. Approximately 20 mg of the sample was placed inside the high pressure steel capsules, then covered with a gold plated sealing and closed tight with the screw-on lid to prevent any leakage. The amount of air trapped inside was kept to a minimum, in order to avoid any influence on the kinetics. After heating to 70 °C, the heat-flow was observed, until the PMMA seemed to be cured to a steady state.

3. Results and Discussion

Beginning with the reference measurements on the MMA system, *Figure 2* illustrates the DSC thermogram under isothermal conditions. The heat flow shows the characteristic behaviour of the inhibited bulk polymerization. Phase 1, ranging from the beginning to approximately 30 minutes, is believed to be predominant by the inhibitor reacting with the gradually decaying initiator and therefore little heat flow is measureable. Reaching the point where the radical creation overcomes the inhibiting capabilites of the inhibitor, the exothermal character of the polymerization reaction starts rather rapidly. This can be oberved at about 30 minutes into the measurement by

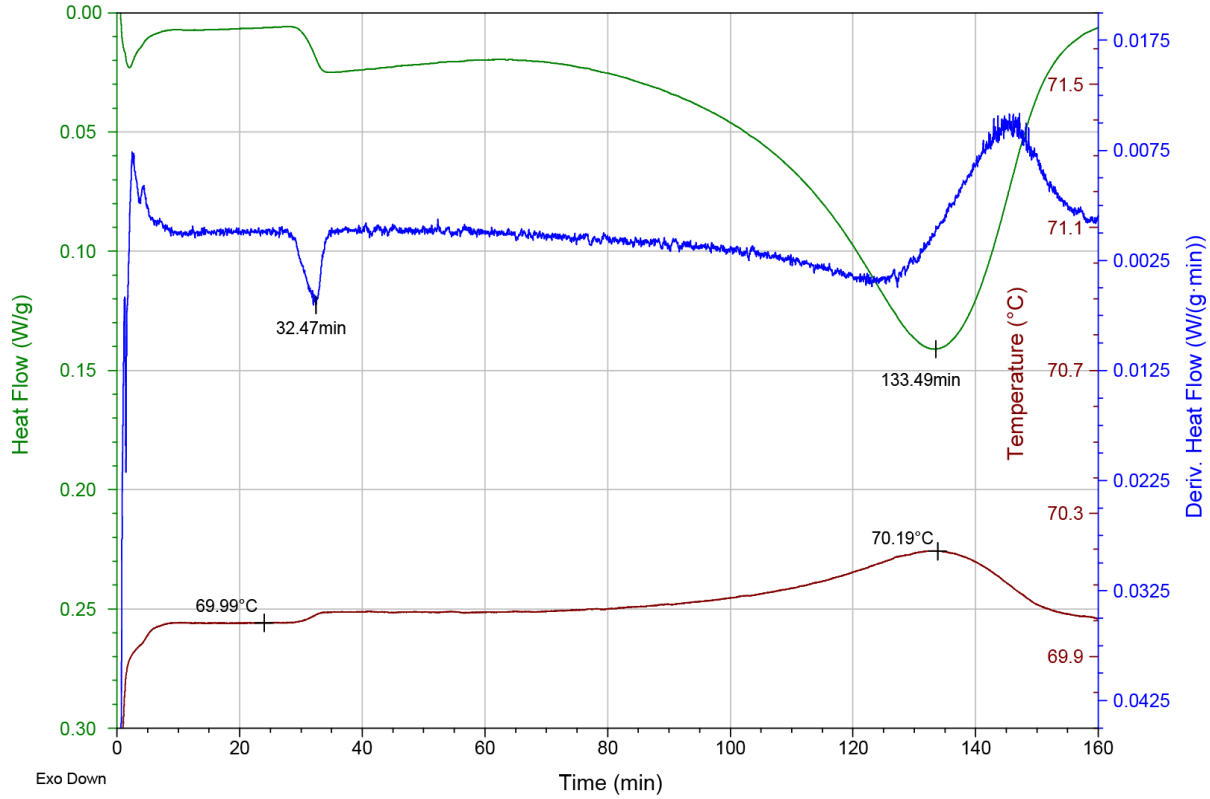

Figure 2: Heat flow (green / top), time derived heat flow (blue / middle) and sample temperature (red / bottom) during the isothermal MMA curing

a step in heat flow and a peak in the time derivative. Due to the exothermic nature, a slight rise in pan temperature can be observed as well, though the extent of this heating up is too small to have any significant effect on the measurements. From around 70 minutes on, the auto acceleration starts to become evident, creating the main peak at 130 minutes.

Taking a look at the excerpts of the Raman spectra for different times (*Figure 3*), several interesting areas can be pointed out. The two desired peaks at 1640 cm^{-1} and 1725 cm^{-1} are well observable and clearly discernable. This was the first and most important criterium for a proper signal evaluation. Furthermore, the shift from a rather dominant C=C (1640 cm^{-1}) at early times to nearly no such peak at later times, already shows the capability of this method for conversion estimations.

Apart from the desired peaks, a wavelike pattern is apparent in the Raman spectra too. Though the exact origin is still under investigation, an explanation might be found from the sample holder rather than the material itself. Harmonics that are created by optical interefences due to the specific gaps between the sealing float glass sheets might give a first deduction. This is supported by the fact, that the pattern is very regular and can be observed throughout the whole spectrum. At starting times, the pattern is better observable, than towards the end of the cure reaction.

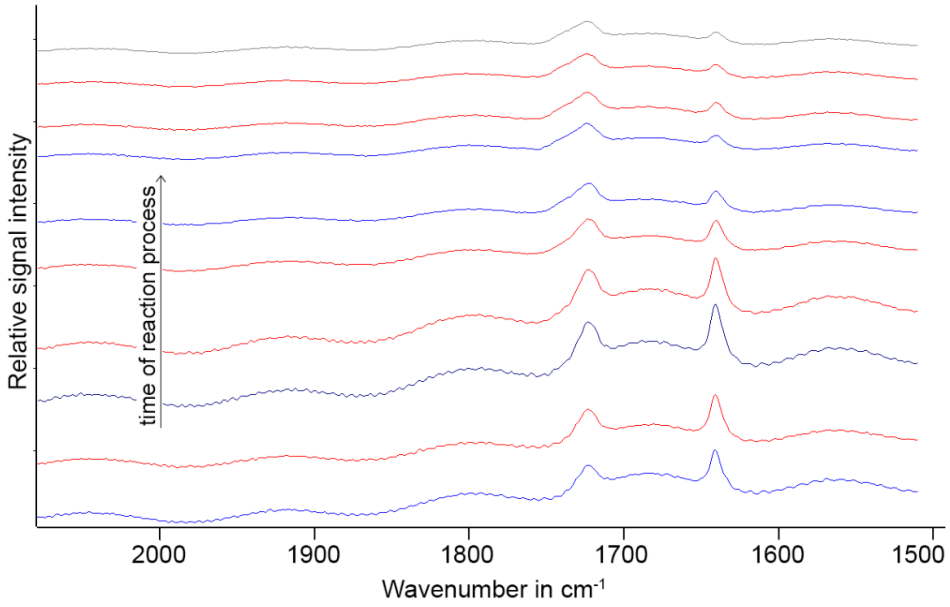

Figure 3: Excerpts from Raman spectra measured during the polymerization

The intensity of the whole spectrum tends to decrease after a certain point, which might be in correlation to the gelation of the polymeric system. A decrease in signal strength due to the mass loss of the volatile MMA could be ruled out, as the sample holders weight was measured before and after the measurement. Sealing was a problem in the initial trials, but has been optimzed through different design iterations in later stages.

To determine the conversion of monomeric MMA to PMMA, the height of the C=C peak at 1640 cm^{-1} was used. Since the spectrum's intensity changes over time, the C=O peak at 1725 cm^{-1} was taken as reference, as the amount of C=O bonds remain unchanged during polymerization. The following formula delivers the degree of conversion C beween 0 and 1, with $P_{C=C;0}$ and $P_{C=O;0}$ as the initial peak heights, as well as $P_{C=C;t}$ ans $P_{C=O;t}$ as the peak heights at the current state of the polymerization:

$$C = 1 - \frac{P_{C=O;0} * P_{C=C;t}}{P_{C=O;t} * P_{C=C;0}} \qquad (1)$$

To automatize the spectrum evaluation up to the point of a conversion graph, with minimizing the effect of the occuring wavelike pattern on the peak hights and the use of a proper baseline, a python script has been developed.

The script first imports the raw data files and tags them with the time-stamp and current temperature reading. For ease and effectiveness of evaluation a soft Savitzky–Golay filter (Package: *savgol_filter* from *scipy.signal*) is applied to the raw dataset. In the following step, rough estimations for the peak heights and baseline orientation are calculated from the lowest and highest points within the area of interest. With these

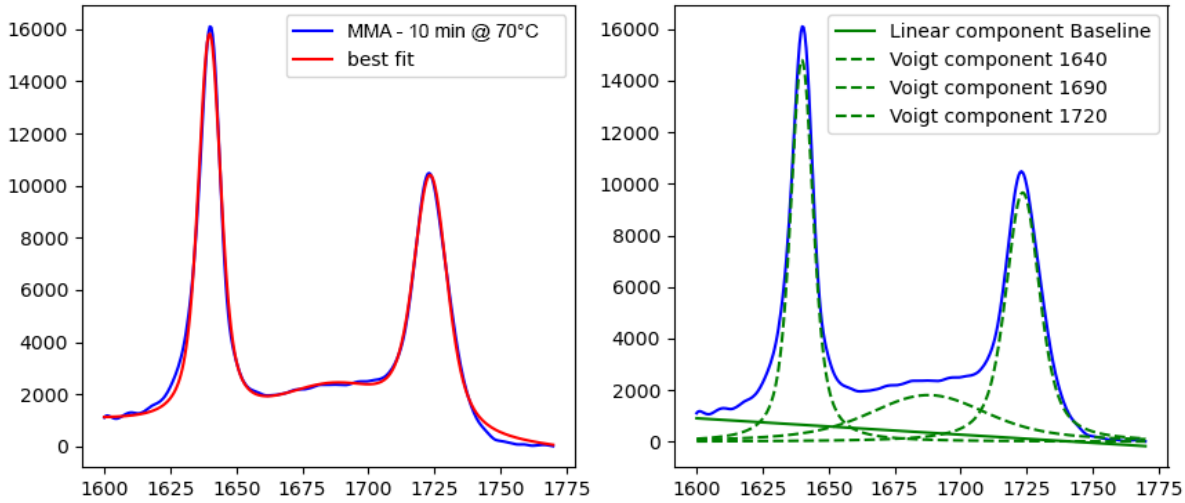

Figure 4: Exemplary fit results as counts over wavenumber - right: single components and smoothed data, left: smoothed data and summed up fit

rough estimations as initial parameters, a linear baseline and three Voigt profiles were fitted to the dataset, as Voigt grants a good variety of parameters to control the shape of the signal to fit. A representative result is presented in *Figure 4*. On the left, the smoothed dataset and the final result of the fitting can be compared. The right graph shows the raw dataset and the four components, which lead to the optimized fit.

It can be seen, that the deconvolution is quite on point and represents the raw data to a very precise extent. At later times, as the overall signal strength reduces, this accuracy tends to decrease a bit. However the results after deconvolution show clearer and more reasonable results, than just the peak intensities from the raw datasets. With the now deconvoluted Voigt components for 1640 cm^{-1} and 1725 cm^{-1}, formula 1 can be applied to get the state of conversion of the current dataset. Carrying out this procedure for each recorded Raman spectrum for every measurement time leads to the conversion plot shown in *Figure 5*. The conversion plot shows four distinctive regions which can be correlated to the following reaction phases:

I. The reaction is predominantly inhibited by the MEHQ and therefore no conversion can be detected. This region corelates nearly perfectly with the DSC measurements.

II. The polymerization of MMA takes place and conversion of C=C bonds is measureable. As the solution has not gelled yet, the reation underlies a more or less linear pathway like shown in [12].

III. The autoaccelerated region, caused by the Trommsdorff effect can be observed from around 80 minutes on. This is a bit later than it was observed in the DSC measurements and finishes at around 130 minutes, which is a bit earlier/quicker.

IV. The steady state region, where close to no increase in conversion is observable, is reached at 130 minutes.

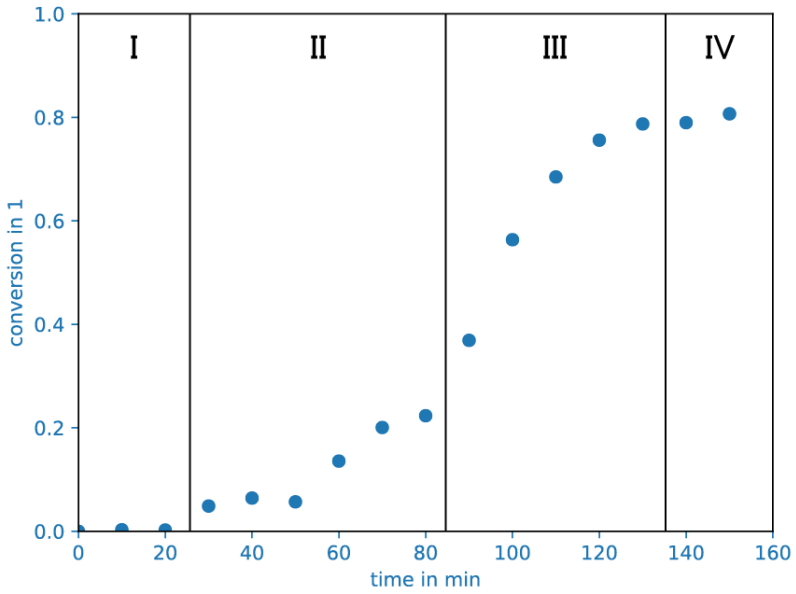

Figure 5: Conversion plot generated from the deconvoluted peak heights

At first glance, the conversion graph that has been calculated from the Raman spectra fits quite well to the DSC measurements and shows the same behaviour as stated by *Jašo et al.* [12]. Especially the first two regions show a remarkable correlation to the DSC data. Taking a closer look into the autoaccelerated region, the difference grows significantly. Especially the early ending of the reaction between III and IV shows a shift of nearly 25 minutes, which can not be reasoned by different sample preparation times. Considering the fact, that the Raman method gives a look inside the chemical structure, the reason to this shift is not believed to be caused by the measurement itself, but by the setup. The low final conversion of slightly above 80 % indicates, that a postcuring of this material under the applied process conditions is needed to remove leftover monomers and shows the benefit of Raman which gives a deeper insight than thermocouples could.

The small DSC pans are optimized to grant an extremly good heat transition from the pan to the measurement apparatus and vice versa. Therefore any heating up, that is caused by the Trommsdorff effect can be compensated very rapidly. The utilization of copper as base material for the sample holder was due to this exact reason, though the size of this sample holder had to be much greater in respect to fit the heating beds size and glass windows. A precise measurement of the copper cores temperature is therefore aimed as further work in order to be able to determine the influence of the heating up due to the autoacceleration. Furthermore, the possibility of copper acting as some kind of catalyst to the reaction is not to be ruled out completely at present. Although copper catalysts are usually utilized in different oxidation states to function, this effect has to be examined in further work.

4. Conclusion

Although the DSC- and Raman-measurements did not show a perfect overlap, it was demonstrated, that Raman is a very powerful tool to determine the current state of conversion in PMMA production. The benefits of an in-line utilization and the minimal changes needed in cast PMMA fabrication as key aspects to this work were demonstrated as well. Further insights in the error, especially in the autoaccelerated region, are needed to understand the reasons, ranging from the temperature control in the Raman chamber to the possibility of copper acting as a catalyst. Furthermore, the applicability after scaling up has to be examined in further work. The main benefits of Raman as a quick as well as facile method of conversion detection and process monitoring were underlined by the fact, that a simple software, like the custom made Raman script, provides a very good approach for data evaluation.

Acknowledgements

I with to express my gratitude to Karin Bode and Gesa Fasse, who helped me a lot in troubleshooting on the Raman sample holder and aided in the experimental Raman measurements, as well as Dr. Ioannis Manolakis for his open ears to any questions on the polymer chemistry. Furhermore, a special thanks goes to *KRD Coatings GmbH*, who helped by providing the material.

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